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Spectrophotometric Study of Os(VI) & Os(VIII) with Some Substituted Benzenesulphonic Acids

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Some substituted benzenesulphonic acids such as metanilic acid, orthanilic acid, 2-aminotoluene-5-sulphonic acid and 3-aminotoluene-6-sulphonic acid have been tried for the spectrophotometric determination of Os(VI) and Os(VIII). Out of these, only orthanilic acid and 2-aminotoluene-5-sulphonic acid are suitable for the spectrophotometric determination of Os(VI) and Os(VIII). Orthanilic acid is most suitable as in this case complete development of colour with osmium takes place within 10 to 15 min and in the acidity range 2*N* to *p*H 3·5. A large number of cations have been found to interfere. However, the interference of these ions can be avoided by prior distillation of osmium as OsO_4.

IN earlier communications[1-3] we have reported some interesting effects that are produced due to introduction of non co-ordinating substituents on organic reagents, in addition to the chelating groups and successfully used these for spectrophotometric determination of some metal ions.

Neither benzene sulphonic acid nor aniline gives any colour reaction with Os(VIII). However, the aromatic compounds containing both amino ($-NH_2$) and sulphonato ($-SO_3H$) groups in the benzene ring, give, colour reactions with Os(VIII). The use of sulphanilic acid (*p*-aminobenzenesulphonic acid) as a spectrophotometric reagent for the determination of Os(VI) and Os(VIII) has been investigated earlier by Majumdar and Sen Gupta[4].

In continuation of these studies, the efficacy of using metanilic acid (*m*-aminobenzenesulphonic acid), orthanilic acid (*o*-aminobenzenesulphonic acid, (2-aminotoluene-5-sulphonic acid, and 3-aminotoluene-6-sulphonic acid for the spectrophotometric determination of Os(VI) and Os(VIII) has been investigated. As a natural corollary, this study is expected to throw light on the effect produced by changing the position of coordinating group, viz. amino group and of introducing a non-coordinating methyl group in sulphanilic acid.

Since Os(IV) did not react with these reagents, studies were carried out for the determination of Os(VI) and Os(VIII).

Metanilic acid gave a red colour with both Os(VIII) and Os(VI), the λ_{max} being at 490 nm. Although, an intense colour developed immediately, its intensity went on increasing with time even after 24 hr. On prolonged standing, the colour changed to reddish black with a shift in λ_{max}. The conditional variations such as those of reagent concentration, acidity and temperature showed no positive effect on the above colour reaction. Thus, metanilic acid proved to be a total failure for the spectrophotometric determination of osmium. Orthanilic acid on the other hand was an effective reagent for both Os(VIII) and Os(VI), and was even better thad sulphanilic acid[4]. The complete colour developen within 10-15 min in the acidity 2*N* to *p*H 3·5 and in this respect it was superior to sulphanilic acid[4] where two hr were required for complete development of the colour in the *p*H range 1·8-3·5. 2-Aminotoluene-5-sulphonic acid gave two different colour reactions with Os(VIII) and Os(VI); a dirty green colour in the acidity 2*N* to *p*H 2·0 and a violet colour in the *p*H range 3·8-5·8. 3-Aminotoluene-6-sulphonic acid did not give any immediate colour with both Os(VIII) and Os(VI). Even after 8 hr of standing the colour intensity was quite insufficient for measurement. The variations in reagent concentration, acidity and temperature on the colour reaction showed this reagent to be unsuitable for spectrophotometric determination of Os(VIII) and Os(VI).

Materials and Methods

The spectra were recorded on a Unicam SP 600 spectrophotometer.

A stock Os(VIII) solution was prepared according to Ayres and Wells[7], and the solution standardized iodometrically[8]. The standard solution of Os(VI) was obtained by reducing the standard Os(VIII) solution with a minimum quantity of aq. ethanol (1:2, v/v). The standard solutions of diverse cations were prepared from their chlorides or nitrates and those of anions from their sodium or ammonium salts; the strengths were determined by standard methods.

One parent solutions of orthanilic acid and 2-aminotoluene-5-sulphonic acid in water were used.

Determination of osmium: (*i*) *Using orthanilic acid* — For Os(VI) or Os(VIII), the colour was developed by adding 200 μg of osmate (OsO_4^{2-}) or osmium tetroxide respectively to 10 ml of the reagent. The mixture was rendered acidic by adding dil. HCl and allowed to stand for 10 to 15 min. After adjusting the acidity between 2*N* and *p*H 3·5, the volume was made up to 25 ml, and the optical density of the

solution measured against the reagent blank prepared. The reddish brown colour of the system corresponding to 8·0 ppm of Os(VI) or Os(VIII) showed maximum absorbance at 490 nm.

(ii) *Using 2-aminotoluene-5-sulphonic acid* — To an aliquot of the standard solution containing 200 μg of Os(VI) or Os(VIII) the reagent solution (5 ml) was added, and the mixture rendered acidic and allowed to stand for 45 min. After adjusting the acidity between 2*N* and *p*H 2·0, and allowing further to stand for 15 min more, it was diluted with water to 25 ml, and the absorbance measured against the reagent blank. The dirty green colour of the system corresponding to 8 ppm of Os(VI) or Os(VIII) showed maximum absorbance at 410 nm.

Osmium(VI) and Os(VIII) under the same treatment as above but between *p*H 3·8 and 5·5 gave a violet colour which had no λ_{max}, however a hump was obtained from 510 to 600 nm.

Results and Discussion

The absorbance of the system with orthanilic acid and Os(VI) or Os(VIII) remained unchanged in the acidity between 2*N* and *p*H 3·5 but decreased outside these limits.

With 2-aminotoluene-5-sulphonic acid the absorbance of the dirty green complex of Os(VI) or Os(VIII) did not change between acidity 2*N* and *p*H 2·0. Above *p*H 2·0 the colour changed to violet and this remained unchanged between *p*H 3·8 and 5·5 with both Os(VI) and Os(VIII).

For complete development of the colour 2 ml of orthanilic acid solution (1·0% w/v) was sufficient for Os(VI) whereas 5 ml of this reagent (1·0% w/v) was required for Os(VIII). However, 3 ml of 2-aminotoluene-5-sulphonic acid solution (1·0% w/v) was sufficient for the development of dirty green coloured complex of both Os(VI) and Os(VIII) in the acidity between 2*N* and *p*H 2·0. The amount of reagent required for complete development of violet colour in the *p*H range 3·8-5·5 for Os(VI) or Os(VIII) was 2 ml (1·0% w/v).

The colour intensity of the complex of orthanilic acid with Os(VI) or Os(VIII) remained constant up to 4 hr while with 2-aminotoluene-5-sulphonic acid, it was stable for 10 hr.

With orthanilic acid Os(VI) and Os(VIII) obeyed Beer's law in the concentration ranges 1·0-18 ppm and 1·0-14 ppm respectively. The optimum concentration ranges evaluated by Ringbom method[9] were 4-14 and 2-12 ppm respectively. The percentage relative errors per 1% absolute photometric error[10] were ±3·1 for Os(VI) and ±2·9 for Os(VIII). The Sandell sensitivities (log $I_0/I = 0{\cdot}001$)[11] were 0·018 μg cm^{-2} for Os(VI) and 0·014 μg cm^{-2} for Os(VIII).

With 2-aminotoluene-5-sulphonic acid the dirty green coloured complex of both Os(VI) and Os(VIII) obeyed Beer's law in the concentration range 1·0-20 ppm with an optimum range 4·0-16·0 ppm. The sensitivities and relative errors were 0·021 μg cm^{-2}, 0·023 μg cm^{-2} and ±3·02 respectively.

The violet coloured complexes of 2-aminotoluene-5-sulphonic acid obeyed Beer's law in the concentration ranges of 1·0-16·0 ppm for Os(VI) 1·0-20 ppm for Os(VIII). The optimum concentration ranges were 4·0-14·0 and 4·0-16·0 ppm for Os(VI) and Os(VIII) respectively. The relative errors per 1% absolute photometric errors were ±2·98 for Os(VI) and +3·01 for Os(VIII). The spectrophotometric sensitivities were found to be 0·020 μg cm^{-2} for Os(VI) and 0·023 μg cm^{-2} for Os(VIII).

Interfering ions — The ions found to interfere even in a ratio 1:1 were Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pt^{4+}, Ru^{3+}, Rh^{3+}, Ir^{4+}, Zr^{4+}, As^{3+}, Sb^{3+}, Cr^{3+}, W^{6+} and U^{6+}. However the interference of these ions may be avoided by prior distillation of osmium as OsO_4.

In the distillation apparatus[12], a solution containing 8 ppm of Os(VIII) was mixed with a solution of the interfering ions. The mixture was treated with 20 ml of 6*M* HNO_3 and was distilled slowly in a current of air for 20 min. The distillate was absorbed in 7·0 ml of 0·07*M* KOH and the colour developed and measured as described above. The average recovery of osmium was 98%.

Only orthanilic acid and 2-aminotoluene-5-sulphonic acid were found to be suitable for the spectrophotometric determination of Os(VIII) and Os(VI).

Although sulphanilic acid[4] combines with osmium (VI)in the metal: reagent ratio 1:2, orthanilic acid and 2-aminotoluene-5-sulphonic acid give no definite composition with osmium (VIII) and osmium(VI). When Job's method of continuous variation[5] and molar ratio method[6] were applied for determining the composition, a black precipitate is obtained instead of colour. Thus sulphanilic acid[4], metanilic acid, orthanilic acid, 2-aminotoluene-5-sulphonic acid and 3-aminotoluene-6-sulphonic acid behave differently with osmium although all of them contain the same colour forming groups in the benzene nucleus.

The coloured products obtained from Os(VIII) and Os(VI) in the presence of an excess of the reagent are similar as is evident from their identical colour reactions, the region of maximum absorption and similar tolerance to *p*H variation.

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